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A facile method to align carbon nanotubes on polymeric membrane substrate

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The alignment of carbon nanotubes (CNT) is the fundamental requirement to ensure their excellent functions but seems to be desolated in recent years. A facile method, hot-press combined with peel-off (HPPO), is introduced here, through which CNT can be successfully vertically aligned on the polymeric membrane substrate. Shear force and mechanical stretch are proposed to be the main forces to align the tubes perpendicular to the substrate surface during the peel-off process. The alignment of CNT keeps its orientation in a thin hybrid membrane by dip-coating cellulose acetate dope solution. It is expected that the stable alignment of CNT by HPPO would contribute to the realization of its potential applications.

Since discovered by Iijima¹, carbon nanotubes (CNT) has attracted increasing attention due to the expectation that its unique structure could bring amazing function in several fields such as electronic elements^{2–4}, hydrogen storage^{5,6}, molecular selectivity^{7–9}, etc. On the other hand, the excellent proprieties of CNT are difficult to be presented at macroscopic scale because of its disordered and bounded state at microscopic nanoscale¹⁰. The desirable orientation of CNT is a key requirement for achieving its potential functions, thus an ideal method to align CNT will extensively push the application of CNT forward. Recently, the incorporation of aligned CNT into matrix has been reported to fabricate composite materials with greatly enhanced performance, such as the CNT membrane for desalination¹¹, and CNT/polymer electrode^{12–14}.

The significance of the CNT orientation is undoubted and deserves exploring. In last two decades, many works have focused on the preparation of aligned CNT. Based on the relative position of CNT to the substrate surface, the orientation of CNT includes: 1) α -alignment, with their axes parallel to the surface, accomplished by electric field¹⁵, shear force¹⁶, cutting¹⁷, etc.; 2) β -alignment, with their axes perpendicular to the surface, accomplished by filtration^{18–20}, CVD-synthesized CNT array^{8,19,21}, anodic aluminum oxide (OAA)-assisted template^{22,23}, electric filed^{15,24,25}, etc. Generally, β -alignment appears much more useful than α -alignment in the specific practical application. This is due to the fact that β -alignment of CNTs is conducive to exploit their special radial properties in a normal plane, such as sieve effect dominated by their serial diameter²⁶ and field effect originated from their excellent conductivity²⁷. Additionally, β -alignment seems much more difficult to achieve compared to α -alignment. The existing techniques are quite limited, either providing a high density of aligned CNT, such as CNT array⁸ and filtration²², or giving a low density of that, such as electric field method²⁸ and micro-fabrication²⁹. OAA-assisted template method^{22,23} does enhance the maneuverability of the alignment and other parameters of CNT, but the strictness of the manipulation and the high cost of materials deemphasize the feasibility of this method in large-scale yield. In the existing methods, most of the aligned tubes have a length of several micrometers (1–5 μm), which is not easy to be inserted into thin membrane layer. Shorter CNT is easier to be embedded into the thin membrane layer but more difficult to be aligned because short CNT is more sensitive to random thermal motion. Moreover, most of the existing methods need a rigid substrate, which limited the application of aligned CNT in the soft materials. For the last several years, no brand-new method has been reported thus it seems that the study of CNT alignment has arrived at a dead end.

In this report, we introduce a new facile method to align CNT vertically and homogeneously on polymeric membrane substrate, which is achieved by easily hot-press combined with peel-off (HPPO, Fig. 1). The hot-press can conglutinate a thin layer of single-walled carbon nanotube (SWNT) in two pieces of polymeric membrane together like a sandwich, while the peel-off separates the two membranes and simultaneously aligns SWNT by the shear force and mechanical stretch. Interestingly, the tubes still remain aligned even after being coated with a layer of polymeric casting solution, showing a potential application of aligned SWNT in the thin membranes.

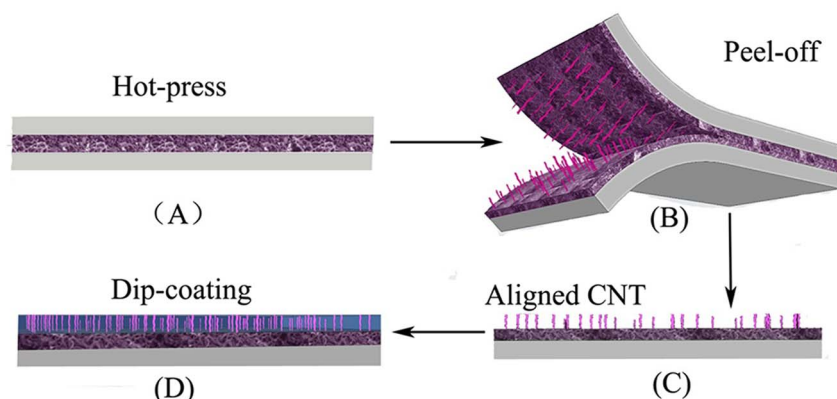


Figure 1 | Schematic of the method to align SWNT by hot-press and peel-off. (A) Deposit SWNT on nylon membrane by spraying uniform suspension. (B) Hot-press the wet PSF membrane on the SWNT/nylon film until dry. 100°C is an appropriate temperature since high temperature will ruin the membrane and lower temperature will decrease the transfer quantity. (C) Peel off the PSF membrane from nylon membrane. (D) Coat SWNT/PSF membrane with cellulose acetate (CA) casting solution.

Results

After the HPPO process, both membranes were fixed on the slope surface of a triangle stage and then investigated by Scanning electron micrographs (SEM). It can be clearly seen from Fig. 2 that SWNT on both of surfaces of polysulfone (PSF) and nylon membranes vertically stood up. On the PSF membrane, it was clearly noted that a lot of tubes were aligned in a quite large area and kept a good and homogeneous distribution on a thin SWNT layer (Fig. 2A). The existence of the SWNT layer will be confirmed by the following transmission electron microscopy (TEM) images. It seemed that the longer tubes dominated the whole surface due to its obvious long structure. Factually, the longer tubes were much less than the short ones in number demonstrated by the same TEM images. On the nylon membrane, tubes were also aligned broadly except in the loose pores, which are the special characteristic of nylon membrane. But it can be still seen that a SWNT layer existed though it was not that complete (Fig. 2B). On the surfaces of both membranes, the height of aligned tubes ranges from 50 to 500 nm, a little shorter than the average length (500 nm) of SWNT in suspension. This could be attributed to the fact that the tubes stood freely but kept a part of their body in the thin layer as a root. Therefore, most of tubes have a shorter height than the average length.

In order to investigate the mechanism of the CNT alignment in HPPO process, two membranes were firstly treated by hot-press, and then these bonded membranes were carefully peeled off but not separated thoroughly from each other. Each of the peeled membrane was fixed on the sample stage by conducting glue with the joint segment exposed to be detected by SEM (Figure 3). In the joint segment, it can be clearly seen that lots of tubes aligned with either both or one of their end-points fixed in an inclined or vertical way.

Some of the tubes were pulled from the SWNT layer, and some of the tubes were quite short but almost vertically aligned. This interesting observation of the SWNT position and distribution between the two membranes gave more sound proof to the following alignment model.

During the hot-press process, SWNT deposited on the nylon membrane would have a strong interaction with the surface of the membrane due to the high temperature process³⁰. As the membranes were peeled off from each other, a slight drag force appeared as explained in Novoselov's experiments³¹. It pulled and aligned each tube vertically tight until one of its end-points was released from SWNT layer. The drag force could be divided into two extreme cases: shear force and mechanical stretch (Fig. 4). When an individual tube is vertically buried and pulled from tube stacks, other tubes serve as a medium which bears some viscosity and provide the shear force to align SWNT perpendicular to the surface of membrane (Figs. 4 A–C). The excellent mechanical properties of tubes guarantee their integrity when pulled out through the SWNT stack³², which is compacted during the hot-press. When an individual tube is horizontally laid with both of its end-points fixed on different sides, the twisted and leaned tube will be stretched and aligned due to the mechanical stretch³³ (Figs. 4 D–F). Actually, the shear force and mechanical stretch is not definitely perpendicular to the surface of membrane due to the existing gap angle between two membranes (Figs. 4 J). However, the small height of the tube limits the magnitude of the gap angle, leading to an angle deviation (AD) of directivity of the shear force which is so small that it can be neglected (Supporting information). In practical experiments, the shear force and mechanical stretch may take effect at the same time (Figs. 4 G–I). Although tubes are not bound to be exactly vertically aligned in principle, it is still

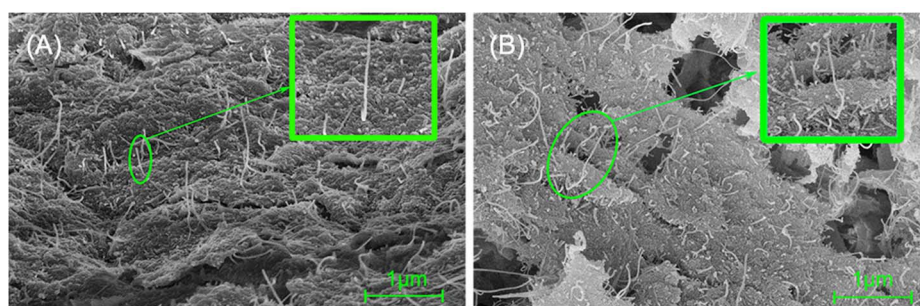


Figure 2 | SEM images of aligned nanotubes on both PSF (A) and nylon membranes (B) after HPPO. Tubes are obvious vertically (β -) aligned in an appropriate density.

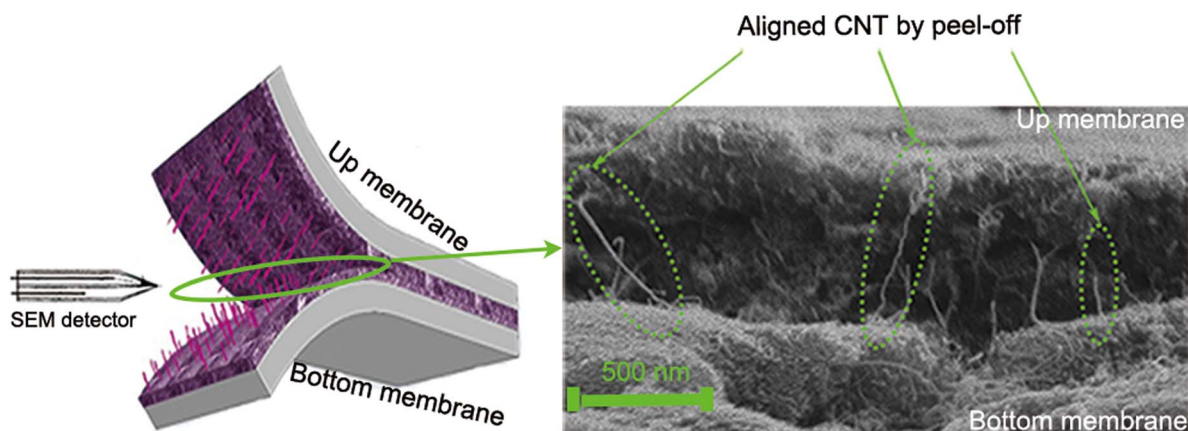


Figure 3 | SEM images of aligned carbon nanotubes in the joint segment between two membranes.

satisfactory to observe the orderly-stood SWNT in microscopic view (Figs. 2).

Since the force existed and worked for the SWNT layer on the surfaces of both membranes, SWNT on both sides were pulled and oriented at the same time as shown in Fig. 2. It is reasonable to consider that a stronger interaction between two surfaces due to a higher temperature and a more powerful press in the hot-press process will result in a higher density of aligned tubes. Therefore, the control over parameters and conditions of the craftsmanship is supposed to determine the desired density and length of nanotubes. However, too high temperature or much excessive press will damage the membranes by sticking them together firmly thus tearing them into pieces when peeled off.

Fig. 5 shows that the alignment of SWNT does not change at all after coated with the CA membrane, indicating that the channel of SWNT is possible to assist the transport feature of membrane. The tubes keep perpendicular to the surface of SWNT layer (thickness ≈ 100 nm) with one of their points planted in the layer. Several tubes can be observed to align throughout the layer in the case that it is long enough. The height of tubes is about 50 to 200 nm and this is consistent with the SEM results. For the tubes morphology on plane surface (Fig. 2), it is quite easy to find a long tube in the view. However, for the tubes morphology on cross section surface (Fig. 5), it seems that shorter tubes are more pervasive. This could be due to that the morphology on cross section is only a small part of that on plane surface. Therefore, short tubes are major components in a given view.

Discussion

By this process, SWNT can be successfully vertically aligned on the polymeric membrane substrate. Furthermore, the alignment of SWNT keeps unaltered in a thin hybrid membrane after dip-coating cellulose acetate dope solution. Obviously, the HPPO method is remarkably expedient in the preparation of vertically-aligned-CNT compared with others for its great simplicity and convenience. This method also indicates that macroscopic manipulation can also realize the microscopic orientation of nanotubes and provides a very promising approach to be well employed in the manufacture of field effect transistor (FET). Inspired by the CNT-based hybrid membranes^{34,35}, this method will realize the alignment of CNT in separation membranes, such as reverse osmosis membranes³⁶, pervaporation membranes³⁷. And the follow-up work must be completed by associated fellows for its convenient manipulation.

Methods

Preparation of aligned CNT film. SWNT was treated in a mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3 : 1) to functionalize them as hydrophilic materials. Uniform SWNT suspension was prepared by dispersing acidulated SWNT in water (10 mg/100 mL), and then ultrasonicated for 20 min to guarantee adequate dispersion, finally centrifuged for 20 min to remove large particles. Tubes have an average length of 500 nm and an average diameter of 10 nm after serial treatment. A nanotube film was obtained by directly dipping the membrane in the SWNT suspension or spraying a certain volume (1.0 mL/cm²) of SWNT suspension on the nylon membrane and then removing the water by vacuum evaporation, leaving tubes twisted variously and piled up randomly (Supporting information). Though it was reported that the shear force could align

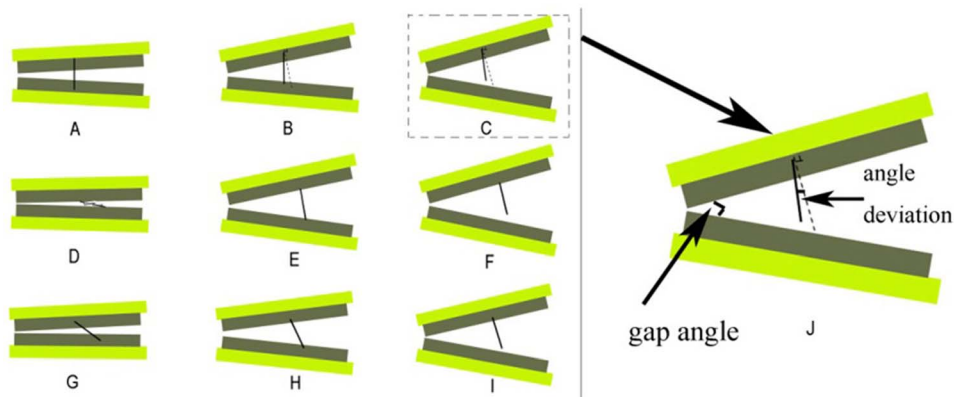


Figure 4 | Schematic illustration of the alignment mechanism of SWNT by peel-off as an example is taken on an individual tube. One extreme case (A–C) is that one tube is fully buried cross stacks of SWNT. The tube is pulled out and aligned perpendicular to the symmetry axis of two membranes. Thus there exists a small gap angle between the direction of SWNT and the normal line of the membrane (J). The other case is that the tube was piled up among stacks (D–F). The twisted tube is stretched straight and aligned before one of its ends is released. As is noted above, gap angle is also existed and negligible. In common case, the tube was pulled and stretched in the same time (G–I).

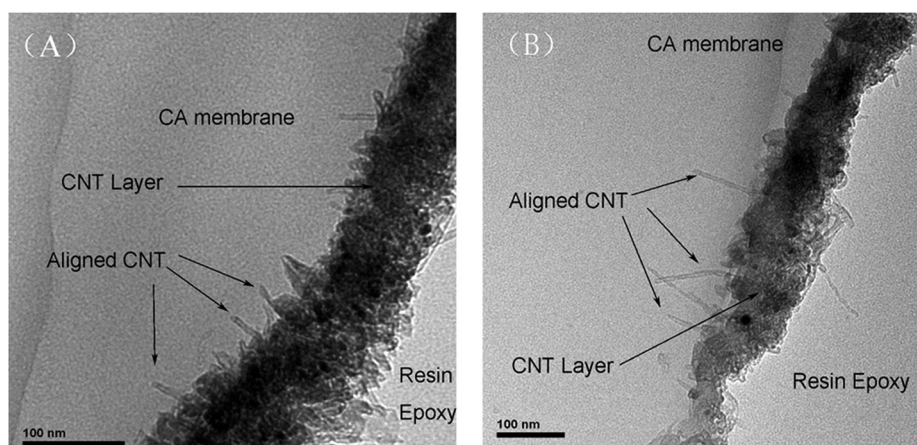


Figure 5 | TEM images of aligned SWNT embedded in the polymeric membrane. (A) Short aligned SWNT is pervasive in this image and some tubes permeate through the black SWNT layer. (B) Long aligned tubes are also observed. In fact, much longer SWNT should exist with a length over 500 nm as manifested by SEM images but it is really difficult to detect them in a small view of TEM images.

nanotubes³⁷, here the force intrigued by the evaporation seems not big enough to align the tubes.

Then the prepared black nylon membrane was then covered by a selected wet PSF membrane (Supporting information), following by hot-press on a Teflon plate at the temperature of 100–120°C and the pressure of ~106 Pa for 10–20 s. After that the nylon membrane was peeled off with great care to ensure the integrity and stain-lessness of both membranes (shown in Fig. 1).

Preparation of aligned SWNT-incorporated membrane. After achieving a good alignment of SWNT on PSF membrane, we coated the SWNT/PSF membrane with the casting solution, which was prepared by dissolving 8 (M/V)% cellulose acetate (CA) in acetone and stirring for two days to insure the solution completely homogenous. Then the wet membrane was exposed in the open air until dry, forming a hybrid polymeric membrane (SWNT-CA) layer.

Characterization of aligned SWNT on the membrane surface. After the HPPO process, both membranes were fixed on the slope surface of a triangle stage. SEM images of both membranes were taken as shown in Figs. 2 and 3. After coating polymer solution, the final hybrid membrane was peeled off from the PSF membrane, embedded in resin epoxy and cut into slices for observation by TEM as shown in Fig. 5.

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Author contributions

H.Z. and L.Z. designed the experiments. H.Z. prepared and characterized the aligned SWNT. H.D. and Z.Z. helped analyze the results. H.C. and L.H. guided the work and analysis. H.Z. wrote the paper. L.Z. revised the paper.

Additional information

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